MAUSAM, 50, 2 (April 1999), 203-210

551.510.534 (9)

Measurement of Ozone at Maitri, Antarctica

V.S.TIWARI

India Meteorological Department, New Delhi-110 003, India

(Received 28 October 1997, Modified 15 June 1998)

सार— भारत मौसम विज्ञान विभाग द्वारा भारतीय इलैक्ट्रो-रसायनिक ओजोन सौन्दे की सहायता से अंटार्कटिका में दक्षिण गंगोत्री में 1987 से और तत्पश्चात् 1990 से (70.7° द.,11.7° पू.) मैत्री में नियमित ओज़ोन प्रोफाइल मापे गए। सतह ओजोन माप भी दक्षिण गंगोत्री में 1989 से और तत्पश्चात् मैत्री में प्रारम्भ किएं गए। दक्षिण गंगोत्री और मैत्री के ओज़ोन सौन्दे आंकड़ों का विश्लेषण किया गया और ओज़ोन छिद्र संरचना का विस्तार से अध्ययन किया गया। शून्य मान के निकट 100 hPa से 30 hPa तक के स्तर के मध्य ओज़ोन की मात्रा में भारी कमी स्पष्ट रूप से देखी गई है। संयोगवश यह एक ऐसा स्तर है जहां सितम्बर-अक्तूबर के अतिरिक्त अन्य महीनों में उच्चमत ओजोन संकेन्द्रण घटित होते हैं। क्षेत्रफल और गहनता में वृद्धि के साथ 1994-95 के दौरान ओजोन छिद्र नितान्त तीव्र पाए गए हैं। अंटार्कटिक ओज़ोन छिद्र 1996 के दौरान भी-पूर्व वर्षों की भांति था। 1995 की घटना का रोचक तथ्य नवम्बर और दिसम्बर में ओजोन छिद्र की विद्यमानता थी। 1995 के दौरान समतापमंडलीय तापमान में परिवर्तनों से इस बात की भी पुष्टि होती है कि 1995 के दौरान शीत कोड भ्रमिल बहुत अधिक शीत थे और ये नवम्बर तक बने रहे।

ABSTRACT. Regular ozone profile measurement over Antarctica has been made by India Meteorological Department since 1987 at Dakshin Gangotri and later at Maitri (70.7°S, 11.7°E) since 1990 with the help of Indian electro-chemical ozone sonde. Surface ozone measurement was also started at Dakshin Gangotri since 1989 and later at Maitri. Ozone sonde data at Dakshin Gangotri and Maitri have been analysed and ozone hole structure has been studied in detail. The drastic decrease in ozone amount is clearly seen between 100 hPa to 30 hPa layer reaching near zero value. Incidently this is the layer where highest ozone concentration occurs during other months except September-October. The ozone hole has been quite severe during 1994-95 with increase in area and depth. During 1996 the Antarctic ozone hole was also similar to previous years. An interesting feature of the 1995 event was the persistence of ozone hole through November & December. Stratospheric temperature changes during 1995 also support that the cold core vortex during 1995 was very cold and persisted up to November.

Key words — Ozone hole, Heterogeneous chemical reaction, Polar vortex.

1. Introduction

Meteorological observational programme has been an integral part of the Indian Scientific Expedition to Antarctica since the first Expedition during 1981-82. Scientific objectives of the meteorological programme has been formulated to meet following requirements.

(*i*) To prepare a climatology of Antarctic region around Maitri (70.7°S,11.7°E).

(*ii*) To study the changes in ozone amount over Antarctica and contribute to the international effort to study ozone hole phenomenon.

(*iii*) Radiation measurements to study the radiation budget and.

(*iv*) To provide forecasting and logistic support to the other participating organizations for the fulfilment of their scientific activities/experiments.

A short description of the ozone measurement programme at Maitri and our assessment about the ozone hole status is described in the present paper. Ozone is a minor constituent of the earths atmosphere, continuously formed at altitude above 30 km from the photo-dissociation of molecular oxygen by solar radiations shorter than 242 nm. Its maximum concentration is localized at an altitude of 20-27 km in the stratosphere. However this minor constituent of the atmosphere has assumed great significance and has been studied in great detail by various scientists because ozone filters out the harmful ultra-violet radiation from the sun light that reaches the earth and thus this thin layer (about 2.5 to 5 mm at STP) provides a shield from uv radiation shorter than 320 nm.

The attention of scientists all over the globe has been further diverted to this minor constituent of the atmosphere because the analysis of ozone data gathered during the last

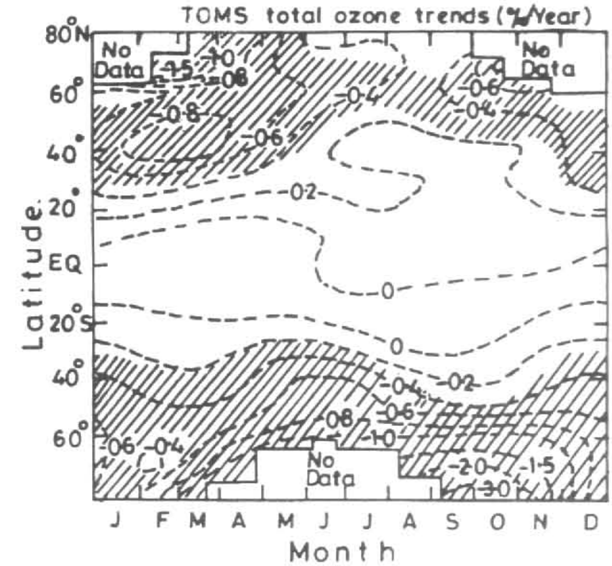


Fig.1. Estimated mean trend (in percent per year) in ozone column abundance as a function of latitude and season. Values deduced from observations by Total Ozone Mapping Spectrometer (TOMS) on board the NIMBUS-7 Satellite (Stolarski *et al.* 1991)

10-20 years (Stolarski *et al.* 1991) suggest a significant world wide decrease in the stratospheric ozone abundance (Fig.1). The most dramatic change has been observed over Antarctica, every spring since late 1970s. The ozone column abundance is dramatically reduced inside the polar vortex. At Antarctic station Halley Bay, for example, the monthly mean ozone column abundance in October was approximately 300 DU in 1960s which has been reduced to around 150 DU in 1990 (WMO/UNEP 1991. Farman *et al.* 1985). The trend in vertical ozone column shows near total disappearance of ozone from 12 to 20 km altitude in September and October. Thus the very thin ozone layer is becoming more and more thinner which may result in allowing the harmful uv radiation to reach earth.

2. Data

Regular measurement of ozone at the Indian Antarctic station-Maitri started since 1987 at Dakshin Gangotri and later at Maitri since 1990 with the help of Indian electrochemical ozone sonde. Weekly ozone soundings are taken throughout the year and during the month of September-October more frequent soundings are taken to keep a close watch on fast depletion of atmospheric ozone. The concentration of ozone at standard and significant level are computed by computer programs. After the preliminary computation each sounding is corrected against the total ozone value.

Apart from vertical column measurement surface ozone is also recorded round the year. A brief account of the results derived from the Indian measurement in respect of Antarctic ozone hole is described in the following sections.

3. Distribution of ozone in the vertical column of the atmosphere

Ozone density in the vertical column of the atmosphere is calculated with the help of weekly ozone sonde ascents at Maitri. These soundings are planned through out the year once a week. However during September to November, when the ozone amount decreases sharply, more frequent observations are also taken. Ozone data is scrutinized and only good soundings are selected for further analysis and publication. Selected ozone profiles from 1987 to 1993 (after correction for total ozone) which have crossed 20 hPa level have been analysed to get a clear picture of changes in ozone hole from single station data. This analysis is presented in Fig.2. We can see from this diagram that the tropospheric ozone below 250 hPa level has remained practically unchanged. The lowest tropospheric values of 10 nb occur between 300 hPa to 500 hPa. The drastic changes in ozone amount can be clearly seen between 100 hPa to 30 hPa year after year. This is the region where maximum ozone (~150-170 nb) is usually recorded as seen from the ozone values occurring from January to June every year. However a region of low ozone (10-50 nb) concentration is also reported at the same level during the month of September-October every year. This is popularly called "Ozone-hole". The diagram shows that the maximum ozone is destroyed in this layer by the heterogeneous chemical reactions arising from photolysis (oxidation) of Chlorofluoro Carbons (CFCs). The photolysis of CFCs(halocarbons) by UV radiation of the sun gives rise to ozone destroying radicals Cl and ClO. Due to this reaction free chlorine (Cl) radicals are set free which act as catalytic agent to convert $2O_3 > 3O_2$. The diagram also shows that the minimum ozone value in this layer which was of the order of 50 nb during 1987-88 has further decreased to 10-5 nb during 1992-93 and the vertical depth of ozone hole has increased in time and space also. Figs. 3(a-g) shows the above features in detail *i.e.* the depth of ozone hole and the period of occurrence has been increasing from year to year. The ozone observations at other stations over Antarctica also support above view that the ozone hole has been increasing in horizontal and vertical area and total column ozone is becoming thinner.

Fig. (4) presents a graph of mean monthly values of ozone observed over Maitri from the ozonesonde data during 1987-93. This diagram shows that :

(*i*) Maximum ozone (~160nb) occurs at the height of 70-80 hPa during April-May. From December to July the average density in this layer is between 130-140 nb.

(*ii*) From August to September the ozone amount in this layer of maximum ozone shows a dramatic decrease from 140-150 nb to 10 nb. The lowest

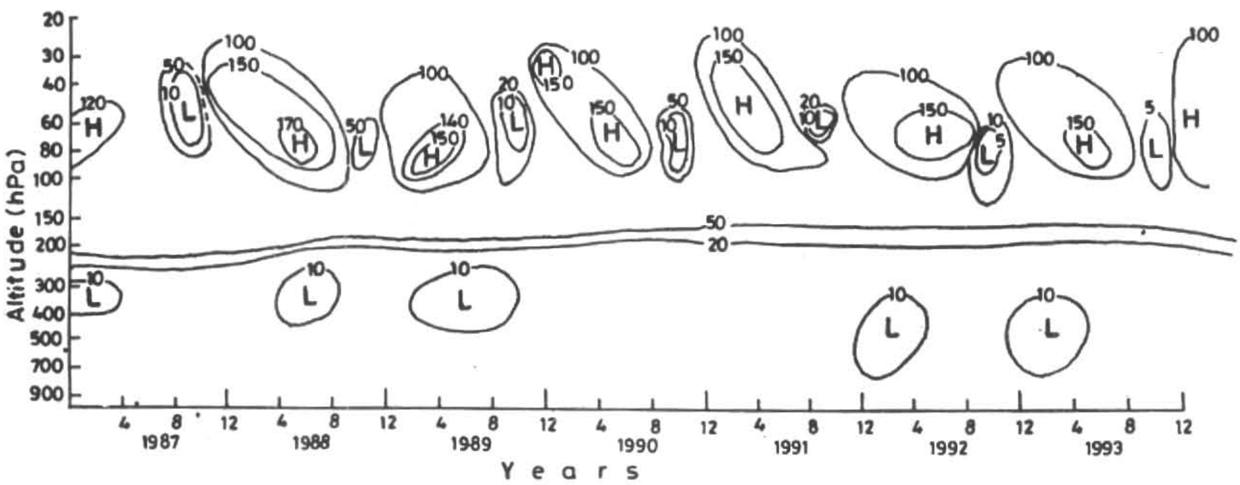


Fig.2. Year-to-year (1987 to 1993) variation in ozone-hole pattern and depth measured at Maitri/Dakshin Gangotri

values continue through October and first half of November. From November to December the fast buildup/recovery of O_3 occurs bringing the ozone amount to near normal in December- January.

(*iii*) During the ozone hole period (September-October) the minimum ozone occurs between 50-90 hPa level which the layer of highest ozone in other months.

(*iv*) The ozone amount in troposphere remains unchanged through out the year.

4. Total ozone

Total ozone distribution over the globe before the occurrence of ozone hole period (1964-1980) is shown in Fig.5(a). The figure depicts the occurrence of maximum ozone (~375-450 DU) over poles during winter hemisphere and minimum ozone over equatorial belt (~250-275 DU). The global average ozone distribution during the period 1984-1993, when ozone hole was detected is also shown in Fig.5(a) and the difference (in percent) can be seen in Fig.5(b) (Bojkov, R.D. *et al.* 1995). It is clear from this diagram that the ozone depletion is taking place at winter poles in both hemispheres, however, the depletion over south Pole is much higher compared to North Pole. The difference poleward of 80° S in October is maximum about -35%. Fig.6 shows the total ozone measured in October since 1956 at Halley Bay by J. Farman and his coworkers. This clearly shows that the total ozone over Antarctica has been steeply falling since seventies.

With above global ozone trend in the background let us examine the changes observed in total ozone at Swoya (Fig.7). Average monthly total ozone value has been calculated for two periods from (1975-83) and from (1984-1994). Prior to 1984 the ozone maxima occurred during the month of November-December and minima in the month of April - May. During the later 1984-1994 the total ozone amounts have decreased appreciably (20-22%) during September-October. During January to July also the ozone values are slightly less. It must be remembered that the ozone decrease has started from 1969-70, therefore the average ozone shown for the period 1975-84 does not actually represent the pre- ozone hole values over Antarctica. The day to day minimum value of total ozone has been reported to be 127 D.U. on 6 October, 1995.

5. Surface ozone

Measurement of surface ozone is also made at Dakshin Gangotri/Maitri since 1989 using the Indian electrochemical surface ozone recorder (Sreedharan, C.R. *et al.* 1993). The surface ozone values show a minimum of the order of 20 ppbv during southern hemisphere summer months (D- J-F) and a maximum value of 40 ppbv during the southern hemisphere winter months of July-Aug (Fig.8). The transition from low summer value to the high winter value occurs during May-June. From October to November there is a sharp fall in the surface ozone values. Fig.(8) shows the density of surface ozone at Dakshin Gangotri along with the measurement at Syowa. The record of surface ozone measured at Syowa and Dakshin Gangotri are very well comparable. The mixing ratio of surface ozone at Pune, a tropical Indian station, is also shown for comparison. Other notable feature of surface ozone in Antarctica is the near absence of a diurnal variation even during summer months. Diurnal variation of surface ozone with a maximum during noon hours is very prominent over Indian stations (Tiwari, V.S. *et al.* 1973). This suggests that the atmosphere over Antarctica is quite stable and diurnal change in temperature does not change the vertical mixing appreciably. Winter maxima appears due to free mixing between troposphere and stratosphere since there is no well defined tropopause over Antarctica during winter. Hourly surface ozone density measured at Dakshin Gangotri is shown in Fig (9). Data

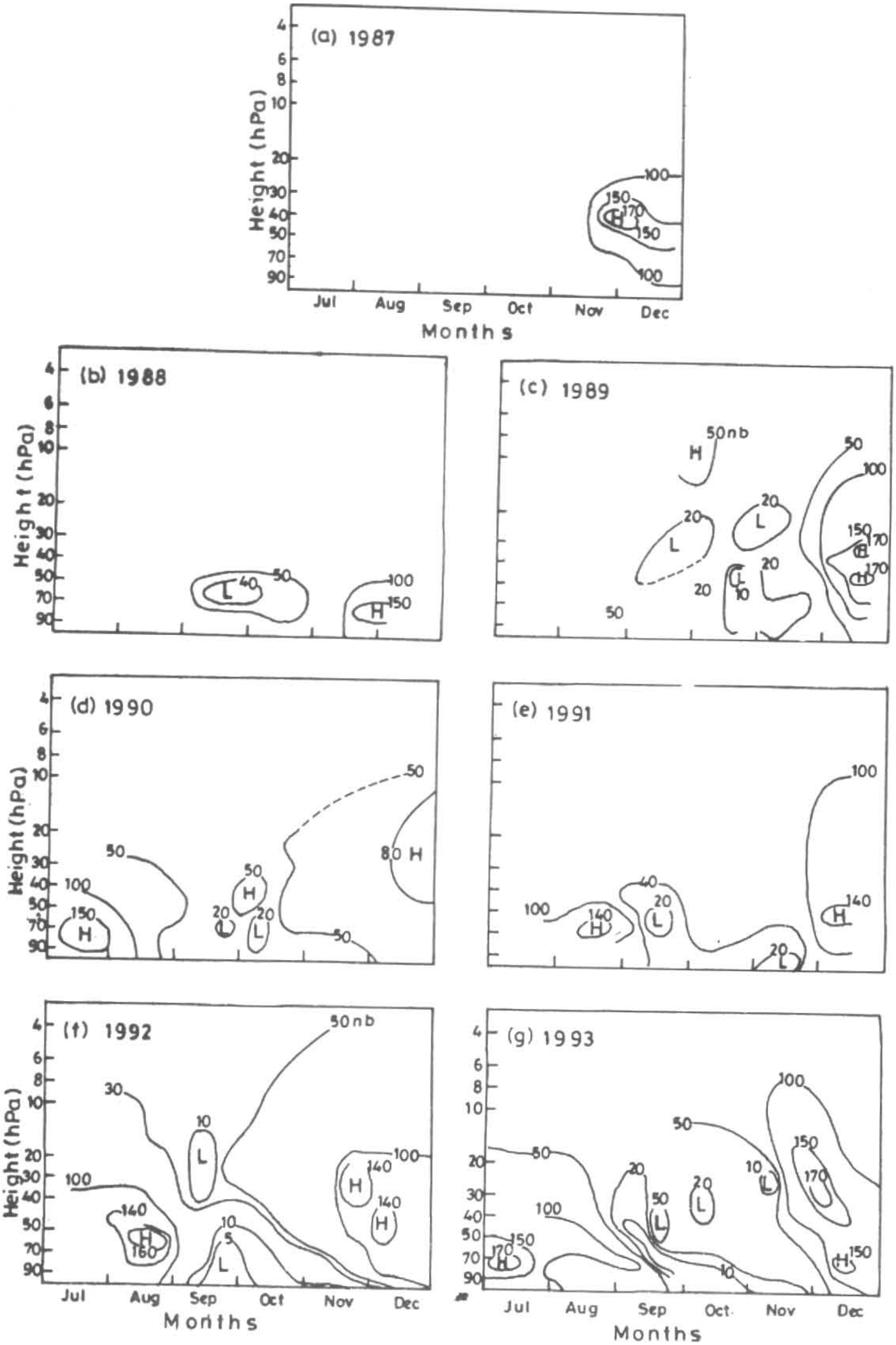


Fig.3. Year-wise analysis of ozonesonde data from 1987 to 1993 (from 100 to 5 hPa)

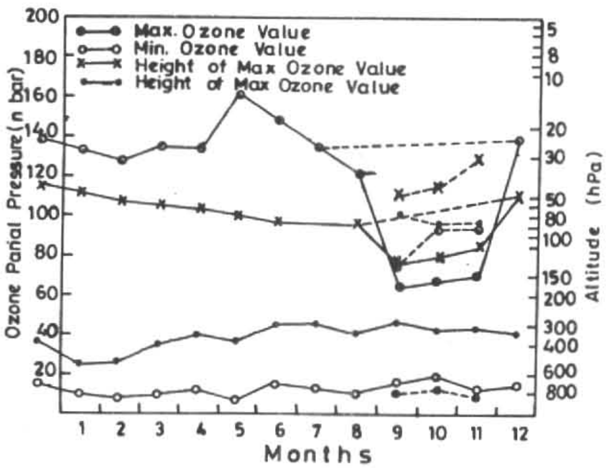


Fig.4. Mean monthly ozone values observed over Maitri/Dakshin Gangotri (1987-1993 data)

recorded at Japanese station Syowa also supports that there is no diurnal variation of surface ozone over Antarctica.

6. Current opinion regarding ozone depletion in Antarctic stratosphere

Farman J.C. *et al.* (1985) from British Antarctic Survey reported that total ozone over Antarctica is decreasing since 1970. Since then the atmospheric scientists have been trying to explain the dramatic reduction in ozone values observed in spring over Antarctica. Chemical mechanisms for ozone destruction generally rely on the presence of "active" chlorine (*e.g.* atomic chlorine, Cl & chlorine monoxide, ClO) in the stratosphere. Homogeneous photochemistry alone can not produce the levels of active chlorine necessary to explain the observed ozone decrease. It was suggested by Solomon *et al.* (1986), Brune *et al.* (1991) that surface catalysed reactions might be source of the required active chlorine. The most important of these "heterogenous" reactions transform the two most abundant inert reservoir of chlorine (HCl and $ClONO_2$) into Cl_2, which photolyses readily to yield active chlorine.

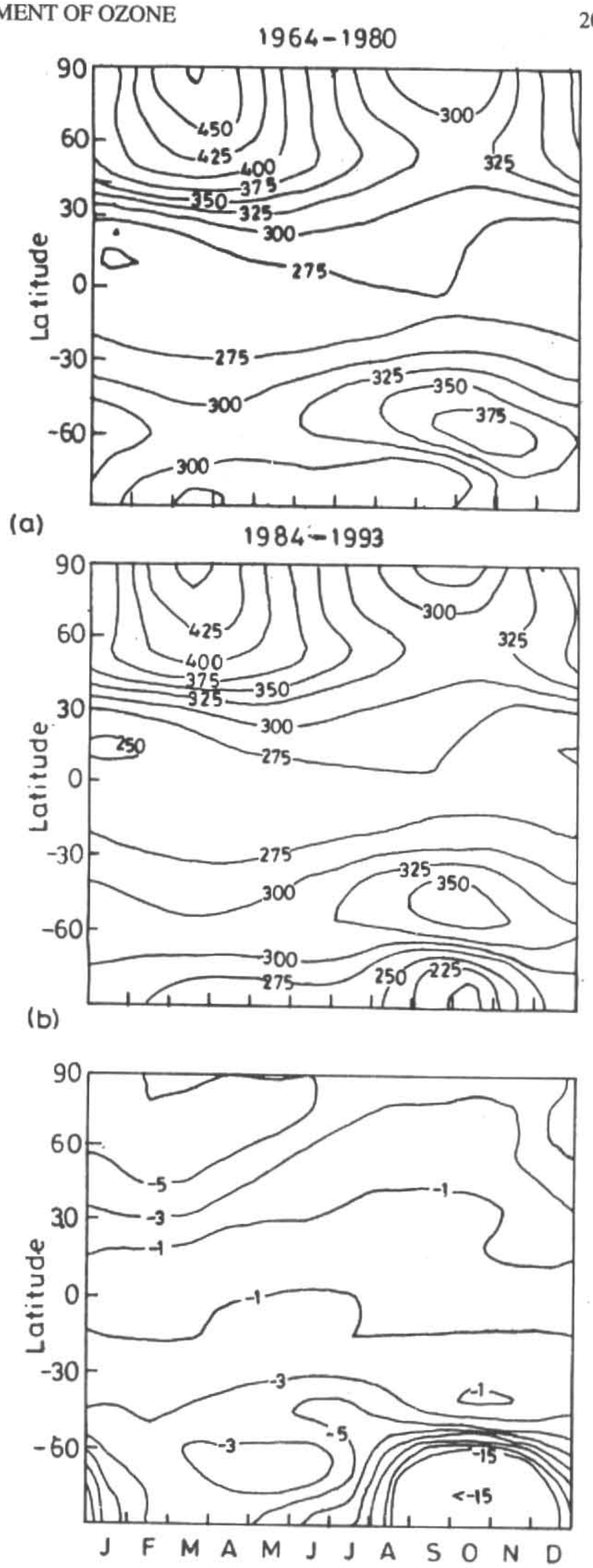
$$HCl + ClONO_2 \rightarrow Cl_2\,(g) + HNO_3(s) \qquad (1)$$

$$Cl_2 + h\upsilon \rightarrow 2Cl \qquad (2)$$

Laboratory studies of reaction (1) have indicated that it proceeds with very high efficiency in the presence of ice (Molina *et al.* 1987, Tolbert, *et al.* 1987, Leu 1988a, Hanson and Ravishankara 1991). Other important reactions taking place on ice surfaces that lead to the release of active chlorine are those between HCl and HOCl (Abbat and Molina, 1992, Hanson and Ravishankara 1992) and between N_2O_5 and HCl (Leu, 1988b, Tolbert *et al.* 1988).

$$HCl + HOCl \rightarrow Cl_2(g) + H_2O(s) \qquad (3)$$

Polar Stratospheric Clouds (PSCs) are now classified in two types- Type I is composed of ice and nitric acid and type II is largely water ice. The work of Molina *et al.* (1987)



Figs.5 (a&b)(a) Variation of total ozone with latitude and season (in m-atm-cm) for time interval 1964-1980 (top) and 1984-1993 (bottom), (b)Difference (in percent) between total ozone values for the two periods (1964-1980) and (1984-1993) reported in Fig.5(a)

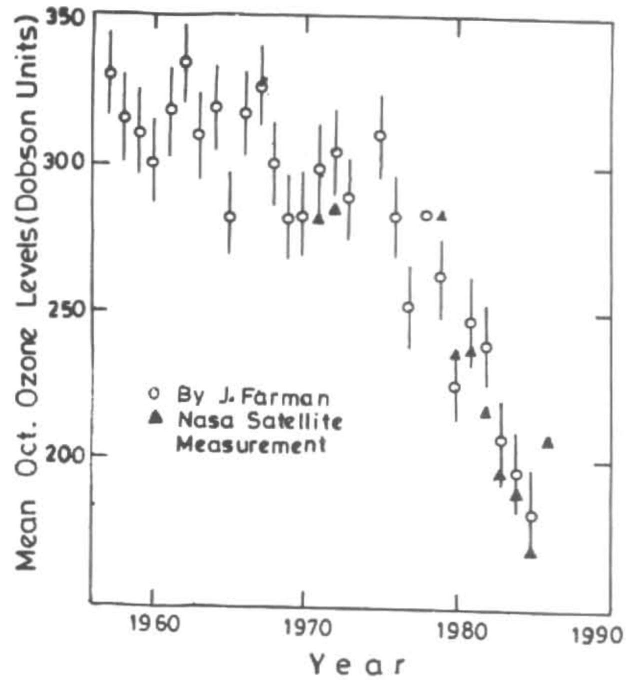


Fig.6. Total ozone amount measured in October since 1956 over Halley Bay

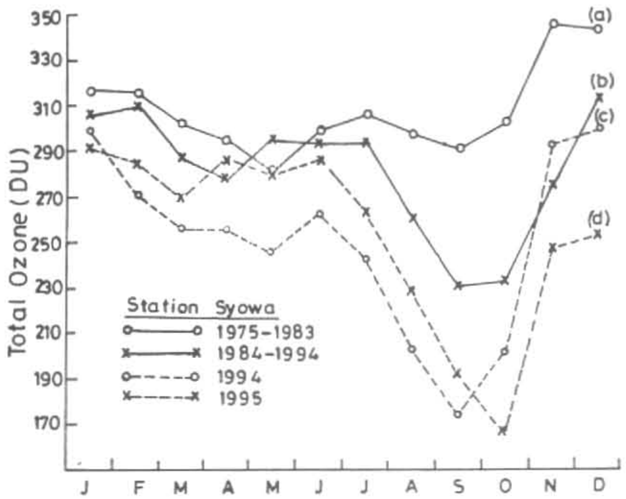


Fig.7. Average monthly total ozone values at Syowa during period (a) 1975-1983 (b) 1984-1994 (c) 1994 and (d) 1995

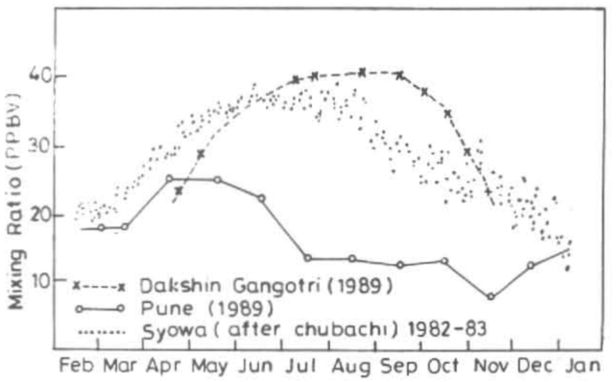


Fig.8. Annual change of surface ozone mixing ratio at Dakshin Gangotri

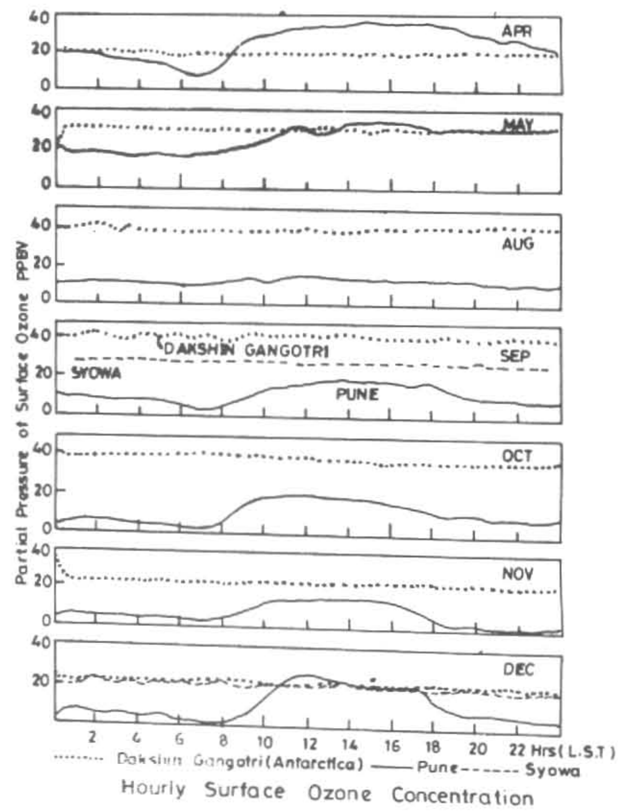


Fig.9. Hourly surface ozone concentration during different months over Antarctica

and Leu (1988) confirm that the reactions (l) and (2) could play an important role in photo-chemical mechanism of ozone depletion in Antarctic spring. However, in order to cause the required ozone loss, the Chlorine produced in above reactions must remain activated. This requires low level of NOx, which would otherwise scavenge active Cl to form $ClONO_2$. Tolbert *et al.* (1988) studied the conversion of N_2O_5 on ice surface at 185°k and reported the following reactions.

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (4)$$

$$N_2O_5 + HCl \rightarrow ClNO_2(g) + HNO_3(s) \quad (5)$$

Reactions (1) to (3) play an important role in release of active Chlorine atoms while reaction (4) and (5) lead to the formation of condensed phase HNO_3 and hence can contribute to denitrification of the Antarctic stratosphere. Reaction (5) could also be a source of $ClNO_2$, which is easily photolysed in the Antarctic spring to form active atomic chlorine.

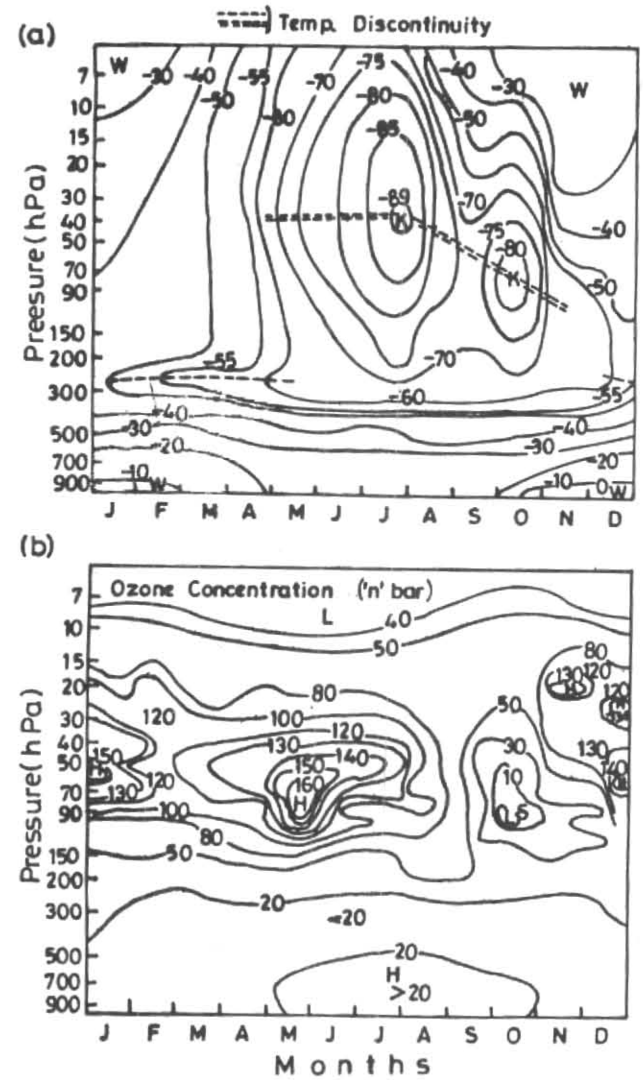


Fig.10. Changes in monthly temperature (a) and ozone (b) profile over Antarctica during 1995

7. Current status of ozone-hole

The nature of ozone hole during 1995 was similar to the severe ones of recent years with ozone dropping to about one third of the pre 1980s values. The maximum area covered by ozone hole in 1995 was about 22 million sq km compared to 24 million sq km during 1994. An interesting feature of the 1995 event was the persistence of hole well into December. The ozone hole phenomenon of 1996 austral spring was in general comparable with that of the past four years, however it has indicated a higher longevity compared to previous years. The ozone hole disappeared only in the first half of December 1996.

Observations from monitoring networks have shown declining growth rate of major ozone depleting substances. Thus the Antarctic ozone hole is not expected to significantly deepen and in the long term (next 20-30 years) is expected to become less severe.

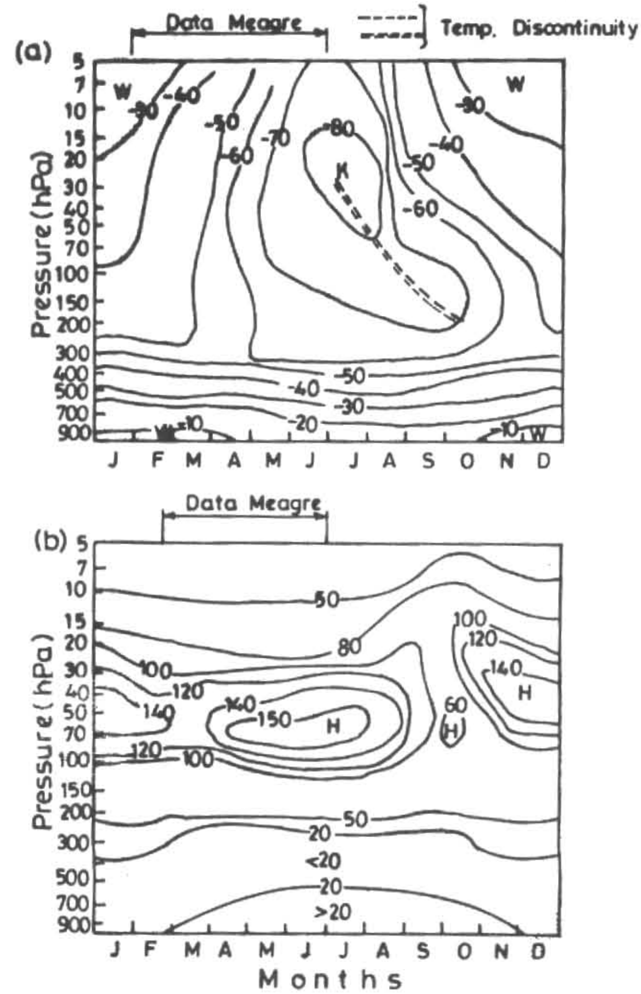


Fig.11. Average changes in monthly temperature (a) and ozone (b) profile over Antarctica during 1988-1990

The vortex of strong westerly winds forms in Autumn and breaks down rapidly in late spring. The extremely cold temperatures within the polar vortex lead to formation of polar stratospheric clouds (PSCs) over large areas in early winter. The rapid photochemical destruction of ozone in the Antarctic stratosphere is due in part to heterogeneous (involving solid and gas) chemical reactions occurring on the surface of ice crystals in PSCs, which release reactive chlorine species that destroy ozone. The chemical reactions are induced by the return of sunlight after the winter polar night.

8. Annual variation in ozone and atmospheric temperature measured over Antarctica

From the preceding discussion and the assessment report of various research scholars/agencies it is established that ozone hole over Antarctic region has been the result of the heterogeneous chemical reactions involving CFCs and other gases, mostly anthropogenic. These gases are pumped into the polar stratosphere from source region through the atmospheric circulation, processes. However, the colder temperatures occurring inside the circumpolar vortex helps in intensification of ozone depletion process. A study of temperature changes in the upper atmosphere along with observed ozone changes has been made and the results are described below.

Figs.10 (a&b) show the changes in ozone and temperature values reported from January to December during the year 1995 from ground (1000 hPa) to 5 hPa level. Monthly mean data of ozone and temperature has been computed from weekly successful ascents. Some interesting results are noticed in the stratosphere. Ozone partial pressure is maximum (about 150-160 nbar) between 90 hPa to 40 hPa level during the period from December to August. Whereas during the month of September and October ozone values are reported lowest (~5 nbar) at the same level. Now let us examine the corresponding changes in temperature. During July- August a cold core polar vortex is formed between 100 hPa and 20 hPa, where coldest temperature is of the order of minus 89°C. From the month of August sun's radiation starts warming the stratosphere, thereby breaking the cold core. Incidently increased uv radiation also take part in heterogeneous chemical reaction and enhance the photo-dissociation of Cl_2 molecules producing active chlorine atoms and chain reaction of ozone destruction begins. It may be seen that during October a secondary cold core system is formed at lower heights (80-90 hPa). The secondary cold core system in October and the lowest ozone concentration (0-5 nbar) are very well colocated in space and time. The centre of cold core system is slowly coming to lower height as month advances through September-October. Ozone minimum also shows a similar pattern slowly descending down from September to October during 1995. Even the 'ozone hole' is seen to protrude during November in 1995. This observation has also been supported by UNEP assessment on the 'state of ozone' in 1995 as described in earlier sections.

To compare the polar stratopheric structure in respect of ozone and temperature distribution during 1995 with earlier years, monthly mean data of temperature and ozone reported during 1988- 90 have also been computed and presented in Figs.11(a & b). This diagram clearly shows that the coldest temperatures during 1988- 90 were of the order of minus 80°C and the cold core vortex was completely broken down during September and first half of October. The corresponding ozone hole is found less severe with lowest ozone value of 60 nbar between layer 50-70 hPa.

The polar stratospheric vortex with its cold lower stratosphere (temperatures below minus 78°C) was dominant over regions with maximum ozone deficiencies. Temperatures below -78°C are known to facilitate the generation of polar stratospheric clouds which, in the presence of halogenated compounds combined with rising solar radiation bring about severe ozone destruction.

References

Abbat, J.P.D. and Molina, M.J., 1992, "The heterogeneous reaction HOCl + HCl→ Cl_2+H_2O on ice and nitric acid trihydrate: Reaction probabilities and stratospheric implications", *Geophy. Res. Lett.*, **19**, 461-464.

Brune, W.H., Anderson, J.G., Toohey, D.W., Fahey, D.W., Kawa, S.R. Johnes, R.L., Mckenna, D.S. and Poole, L.R., 1991,. "The potential for ozone depletion in the Arctic Polar stratosphere", *Science*, **252**, 1260-1266.

Bojkov, R.D. and Fioletov, V.E., 1995, "Estimating the global ozone characteristics during the last 30 years", *Jr. Geophys Res.*, **100**, D8, 16, 537-551.

Farman, J.C., Gardiner, B.G. and Shanklin, J.D., 1985, "Large losses of total ozone in Antarctic reveal seasonal ClO /NO interaction", *Nature*, **315**, 207-210.

Hanson, D.R. and Ravishankara, A.R., 1991. "The reaction possibilities of $ClONO_2$ and N_2O_5 on 40 to 75% sulphuric acid solutions", *Jr. Geophys. Res.*, **96**, 17, 307-314.

Hanson, D.R. and Ravishankara, A.R., 1992. "Investigation of the reactive and non-reactive processes involving $ClONO_2$ and HCl on water and nitric acid doped ice", *Jr. Phys. Chem.*, **96**, 2682-2691.

Leu, M.T., 1988 (a), "Heterogeneous reactions of N_2O_5 with H_2O and HCl on ice surfaces — Implications for Antarctic ozone depletion", *Geophys. Res. Lett.*, **15**, 851-854.

Leu, M.T., 1988 (b), "Laboratory studies of sticking coefficients and heterogeneous reactions important in the Antarctic stratosphere", *Geophys Res. Lett.*, **15**, 17-20.

Molina, M.J., Tso, T., Molina, L.T. and Wang, F.C.Y., 1987, "Antarctic stratosphere chemistry of chlorine nitrate, hydrogen chloride and ice : Release of active chlorine", *Science*, **238**, 253- 257.

Solomon, S., Garcia, R.R., Rowland, F.S. and Wuebbles, D.J., 1986, "On the depletion of Antarctic Ozone", *Nature*, **321**, 755- 758.

Sreedharan, C.R., Russel, D.G. and Basarkar, S.S., 1993, "Surface ozone measurements from Dakshin Gangotri, Antarctica, *Current Science.*, **64(9)**, 632-634.

Stolarski, R.S., Bloomfield, P., Mopeters, R.D. and Herman, J.R., 1991, "Total ozone trends deduced from Nimbus, 7 TOMS data", *Geophys Res. Lett.*, **18**, 1015-1018.

Tiwari, V.S. and Sreedharan, C.R., 1973, "Ozone concentration studies near the ground at Poona - Part-I - Diurnal, seasonal and other time variation and ozone flux measurement", *Ind. Jr. Met. & Geophys*, **24**, 4, 353-362.

Tolbert, M.A., Rossi, M.J., Malhotra, R. and Golden, D.M., 1987, "Reaction of chlorine, nitrate with hydrogen and water at Antarctic stratospheric temperatures, *Science*, **238**, 1258-1260.

Tolbert, M.A., Rossi, M.J. and Golden, D.M., 1988, "Antarctic ozone depletion chemistry — Reactions of N_2O_5 with H_2O and HCl on ice surfaces", *Science*, **240**, 1018-1021.

Tiwari, V.S. and Peshin, S., 1995, "A prominent maximum in surface ozone concentration during winter months at Pune (India)", *Mausam*, **46**, 2, 155-162.

WMO/UNEP, 1991, "Scientific assessment of stratospheric ozone: 1989", global ozone research and monitoring project, Report No. 20, WMO, Geneva.